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MECHANICAL PROPERTIES OF COATED TITANIUM BETA-21S  
AFTER EXPOSURES TO AIR AT 700 AND 800°C

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Abstract

Mechanical properties of Beta-21S (Ti-15Mo-3Al-2.7Nb-0.2Si, wt%) with glass, aluminide, and glass-on-aluminide coatings less than 3- $\mu$ m thick were studied. Coatings were deposited by sol-gel processing or electron-beam evaporation onto 4.5-mil (113- $\mu$ m) thick Beta-21S sheet from which, after oxidizing in air at 700 or 800°C, tensile test specimens were machined. Plastic elongation was the most severely degraded of the tensile properties; the glass-on-aluminide coatings were the most effective in preventing degradation. It was found that oxygen trapping by forming oxides in the coating, and reactions between the coatings and the Beta-21S alloy played significant roles.

## Introduction

Surface oxide formation and oxygen dissolution (to form oxygen interstitials in the alloy) are concurrent oxidation processes in titanium alloys. At low temperatures, oxide formation is the dominant process and the oxide that forms is protective, corrosion resistant, and inert to many forms of chemical attack. At higher temperatures ( $> 400^{\circ}\text{C}$ ) oxygen dissolution increases in importance because it comes to dominate the oxidation kinetics (ref 1 & 2), gives rise to interstitial hardening, and stabilizes the alpha phase. The latter factors have a considerable influence on the mechanical properties of the alloy including tensile strength, ductility, and elastic modulus. Ductility is the first and most seriously affected of these properties, and its loss can be taken as a sign that oxygen interstitials have formed.

The role of nitrogen, during oxidizing exposures in air, is currently uncertain: nitrogen is known to behave similarly to oxygen and with similar effects on the ductility of the alloy, but whether it reacts with titanium alloys in the presence of oxygen is not clear. In any case, to prevent embrittlement of the alloy, interstitials of both elements must be kept from forming, and this can be accomplished with coatings by two approaches: 1) by blocking transport across the coating or 2) by trapping these elements as oxides or nitrides within the coating.

Beta-21S (Ti-15Mo-3Al-2.7Nb-0.2Si, wt%) is a metastable beta titanium alloy and is considered, on the basis of fabricability, strength, density, and oxidation resistance, to be a promising candidate for aerospace applications. The oxidation resistance of Beta-21S is significantly better than Ti-15V-3Cr-3Sn-3Al and somewhat better than commercial-purity (cp) titanium (ref 3).

Beta-21S is now being evaluated for use in hypersonic-vehicle airframes as a composite-matrix material. This would involve frequent short-duration exposures to air at  $816^{\circ}\text{C}$  ( $1500^{\circ}\text{F}$ ) where oxidation occurs rapidly (ref 4). The need for coating Beta-21S when used in this environment is evident, and it is of interest to learn which coating strategies will be most successful. Glass coatings, which block transport across the coating, are representative of one strategy, and aluminide coatings, which trap oxygen by forming aluminum oxide, are representative of a second strategy. In this paper, the effect of glass and aluminide coatings, singly and in combination, on the oxidation and mechanical properties of Beta-21S is reported.

## Procedure

Mill-annealed, 4.5-mil Beta-21S sheet (see chemical analyses in Table I) was cut into 1.5×5-in. panels with the longer dimension parallel to the rolling direction of the sheet. The panels were cleaned with a detergent, rinsed with acetone followed by methanol, blotted dry, and baked for 30 min at  $90^{\circ}\text{C}$ .

The aluminide coatings were formed by depositing  $1\text{ }\mu\text{m}$  of aluminum by electron-beam evaporation, and converting it to  $\text{TiAl}_3$  by annealing for 8 h at  $621^{\circ}\text{C}$  in a vacuum furnace. This heat treatment produced in the alloy a basket-weave alpha-plus-beta microstructure.

The glass coatings were silicophosphates applied by a sol-gel process (ref 5) and cured for

Table I. Chemical Analyses of the Titanium Beta 21-S Material

Sample	Fe	Mo	Al	Nb	Si	C	O	N	H
Ingot, Top*	0.088	16.8	3.18	3.00	0.16	0.018	0.127	0.005	—
Ingot, Bottom*	0.120	15.8	2.95	2.88	0.23	0.026	0.114	0.005	23 ppm
As-Received Sheet	0.130†	15.3†	2.90†	2.97†	0.16†	0.035‡	0.148‡	0.038‡	103 ppm§

\* Ingot chemistry reported by TIMET for Heat G-1664

† By direct-current plasma (DCP)

‡ By combustion thermal-conductivity

§ By combustion thermal-conductivity

a total time of 40 min at 650°C. The process produced in the alloy a very fine, strongly oriented alpha-plus-beta microstructure.

The glass-on-aluminide coatings were formed by applying glass coatings to completed aluminide coatings. The resulting microstructure of the alloy was identical to that of the aluminide coated material.

Continuous thermal exposures were conducted in air at atmospheric pressure by introducing the specimens into furnaces preheated to the test temperature, and by air cooling at the end of the test exposure to minimize the time at temperatures where the omega phase might form.

After exposure, three tensile-test specimens were cut from each panel and machined to the specifications of ASTM Standard E8 (ref 6): the width of the reduced section was 0.250 in. and the length was 1.25 in.

The specimens were loaded in tension until failure occurred. Back-to-back extensometers with a 1.000 in. gage length were used to measure strain. For determining yield, an 0.005 in./min cross-head-deflection rate was used until 5% total strain when the cross-head-deflection rate was increased to 0.05 in./min for the remainder of the test. Yield strengths were determined by the 0.2% offset method and elastic moduli by linear regression over the portion of the stress-strain curve between 0 and 0.5% total strain. Metallurgical specimens were prepared by sectioning the exposed foils and mounting them in a thermosetting medium. The metallurgical specimens were attack-polished using Kroll's reagent and a colloidal-silica slurry.

### Results and Discussion

Reduced oxygen weight gains and retained mechanical properties are benefits that a coating system is expected to provide. In a general sense, these two are related, but the degree of correlation depends on the coating type and the alloy's thermal stability. If the coating actively forms oxides, large weight gains may not imply degradation of properties. If the alloy's thermal stability is poor, changes unrelated to oxidation may be observed in the mechanical properties.

#### Oxidation Effects on Uncoated Beta-21S

Uncoated Beta-21S was tested to establish a baseline for evaluating the coatings and for distinguishing between oxidation and thermal exposure effects. In figure 1 are the

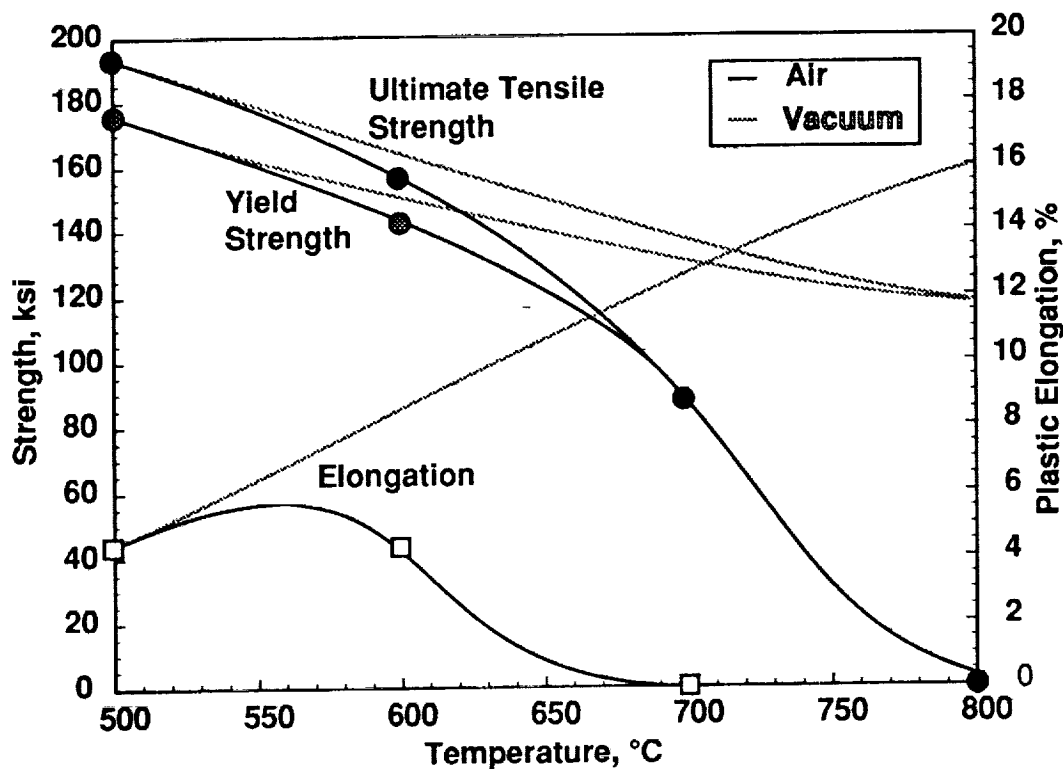


Figure 1. - Room-temperature mechanical property data for uncoated Beta-21S after 12 h exposure to air. The vacuum data (ref 3) shows the effect of thermal exposure, and the difference between air and vacuum shows the effect of oxidation.

room temperature ultimate tensile strengths (UTS), yield strengths (YS), and plastic elongations for 4.5-mil sheet, initially in the beta-annealed condition, after 12 h in air (this study) or 10 h in vacuum (ref 3).

At 500°C, the agreement between the vacuum and air data showed that oxidation in this exposure was not significant. At 600°C, the UTS and YS were almost equal for the vacuum and air exposures, but the difference in plastic elongation indicates a significant loss of ductility caused by oxidation. There was a complete loss of ductility and a considerable reduction in UTS and YS at 700°C due to oxidation. At 800°C, the material exposed in air was very fragile: all specimens broke while being prepared for testing.

#### Effect of Coatings on Ultimate Tensile Strength

Except for cases of complete coating failure, the UTS of coated Beta-21S was relatively insensitive to oxidizing exposure (see figure 2). A small decrease in UTS, seen in all coated material during the first few hours of exposure, was an aging response associated with changes observed in the microstructure.

The UTS of the glass-coated material was consistently higher than the UTS of aluminide-coated or glass-on-aluminide-coated material. This was attributed to the very fine, highly oriented alpha-plus-beta microstructure of the glass-coated material.

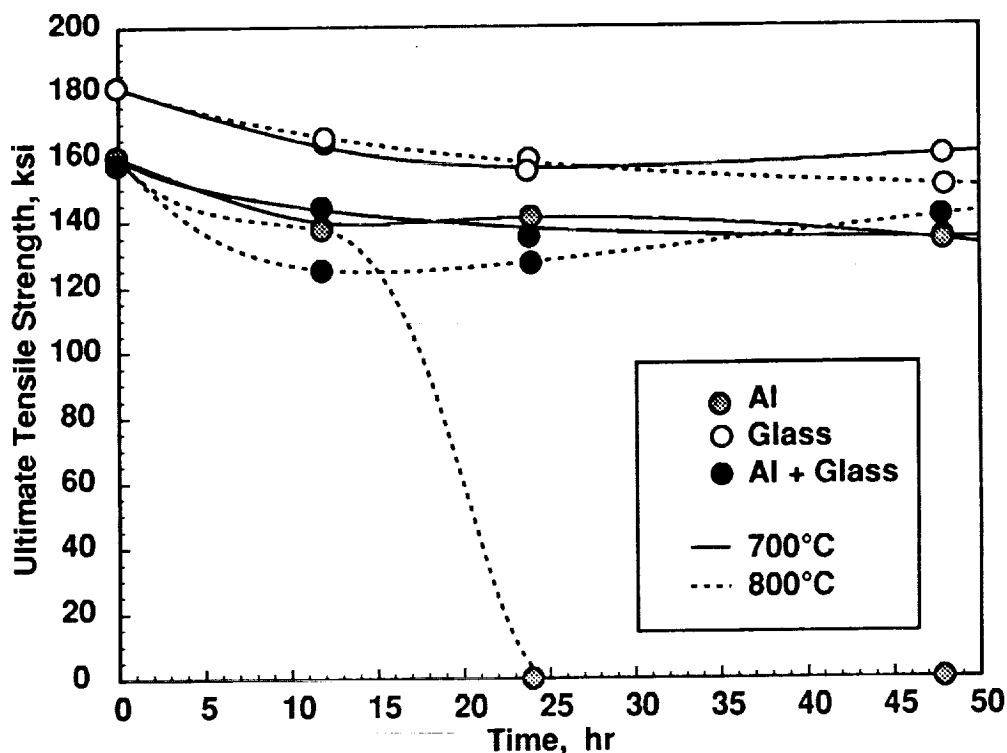


Figure 2. – Room temperature ultimate tensile strengths for coated 4.5-mil Beta-21S sheet after air exposures.

The only serious loss of strength was in the aluminide-coated material at 800°C after 24 and 48 h where the material proved to be very fragile: all of the specimens broke while being prepared for testing.

#### Weight Gains and Plastic Elongation at 700°C

The oxygen weight gains at this temperature for all coated materials were small (see figure 3). All of the coated material showed significantly less weight gain than the uncoated material: after 12 h there was at least an order of magnitude difference. The low weight gains imply that all of the coatings were effective in limiting the entry of oxygen (and nitrogen) from the atmosphere.

While the precise dependence of plastic elongation on oxygen weight gain had not been established for 4.5-mil Beta-21S sheet, prior experience indicated that weight gains of less than  $70 \mu\text{g}/\text{cm}^2$  should have only a minor effect. Consequently, it was expected that the ductility of all the coated material at 700°C would not be excessively degraded. In fact the plastic elongation of material with aluminide or glass-on-aluminide coatings were consistently high, but the plastic elongation of material with glass coatings steadily declined (see figure 4). This decline was attributed to oxygen interstitials generated by reactions between the oxygen-rich glass and the titanium alloy.

#### Weight Gains and Plastic Elongation at 800°C

The oxygen weight gains for the glass and glass-on-aluminide coatings exposed at 800°C

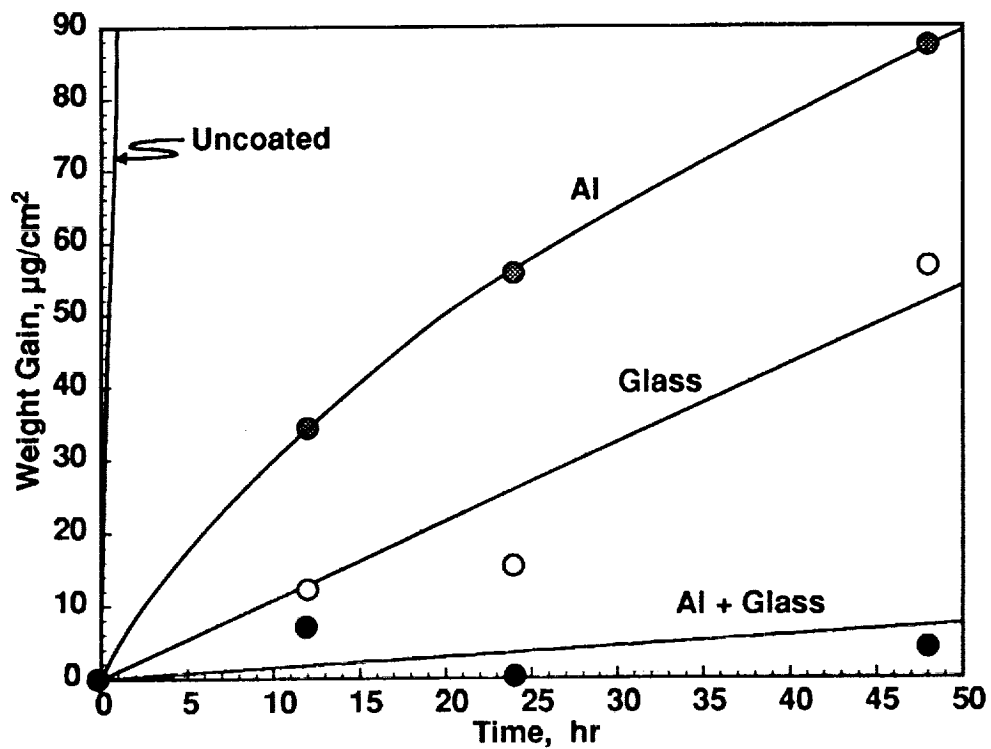


Figure 3. - Oxygen weight gained during 700°C air exposures of coated Beta-21S.

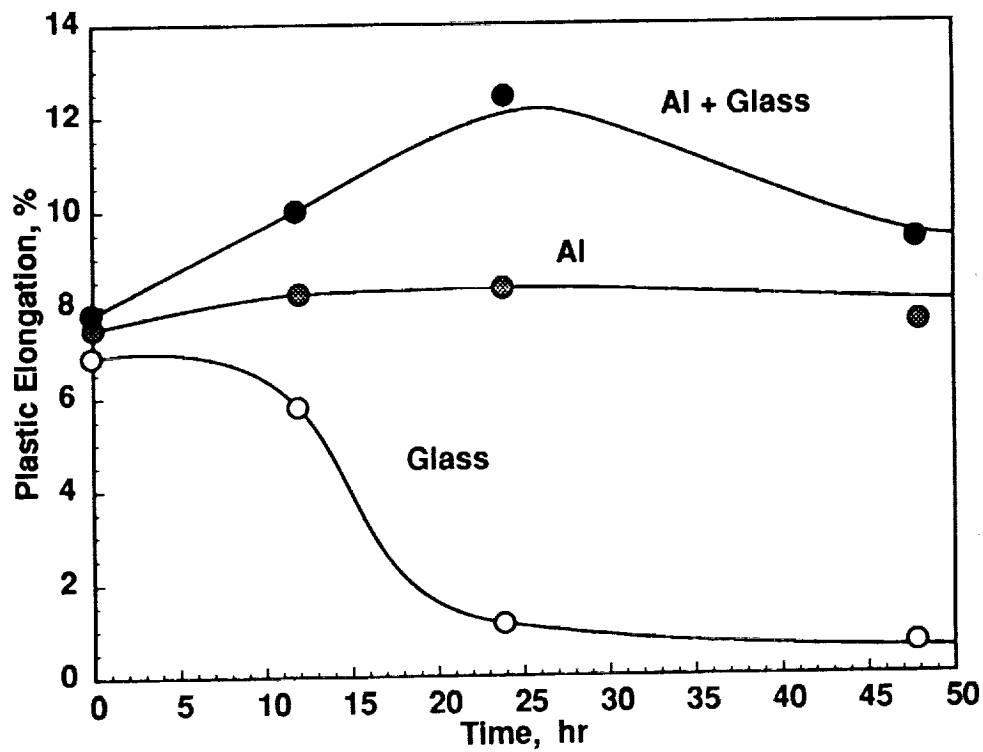


Figure 4. - Room-temperature ductility after 700°C air exposures of coated Beta-21S.



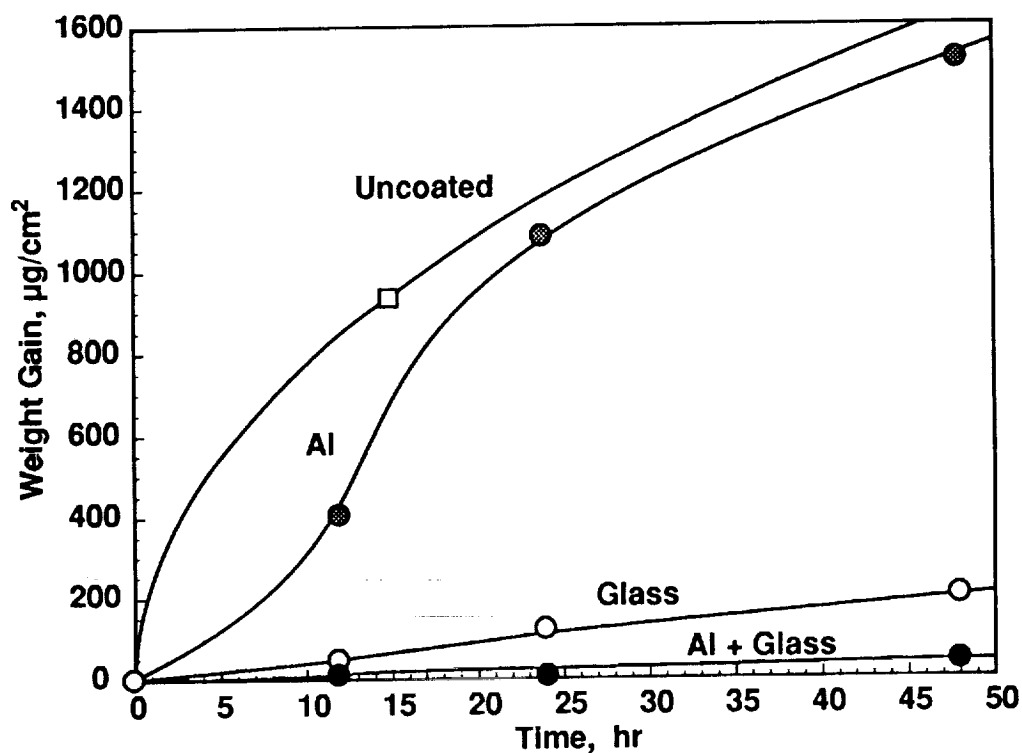


Figure 5. - Oxygen weight gained during 800°C air exposures of coated Beta-21S.

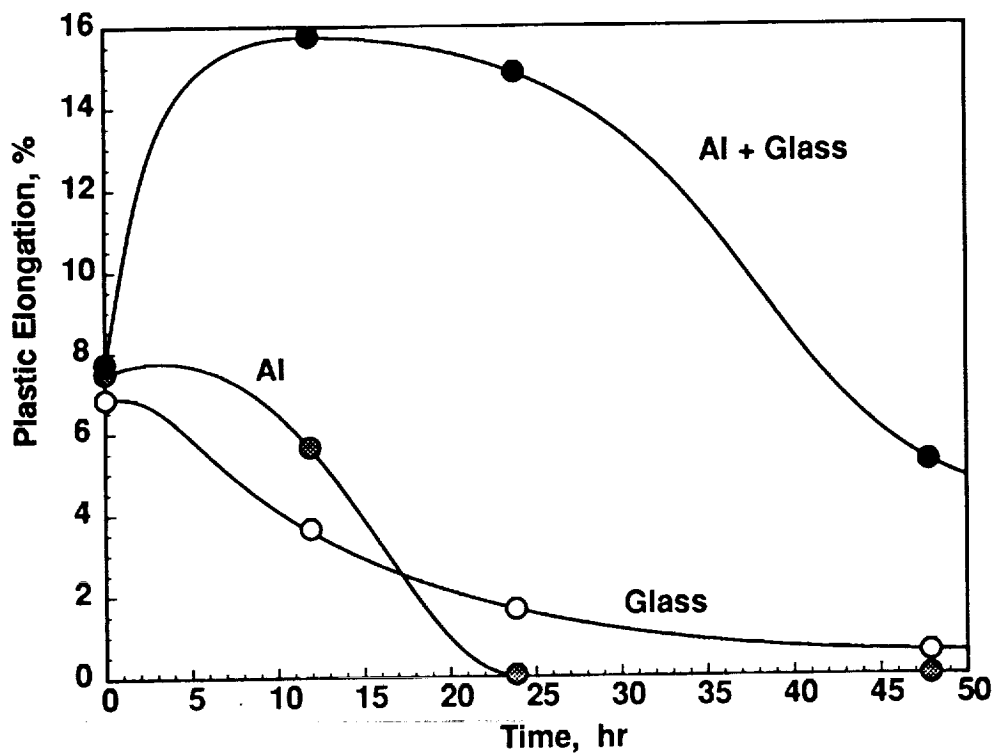


Figure 6. - Room-temperature ductility after 800°C air exposures of coated Beta-21S.

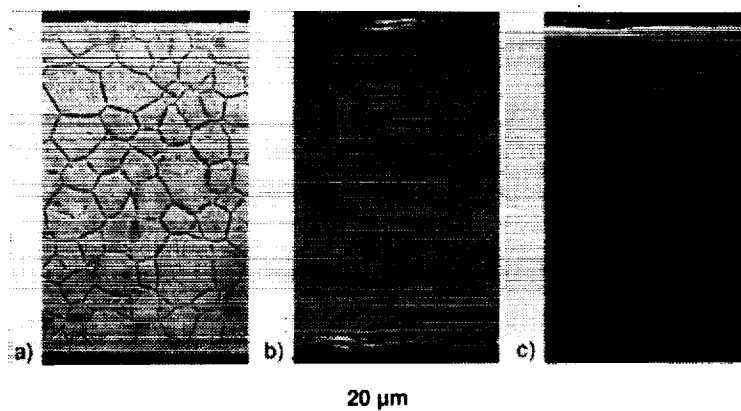


Figure 7. – Scanning electron micrographs of coated Beta-21S in cross section after 12 h at 800°C: a) glass coated; b) aluminide coated; c) glass-on-aluminide coated.

were small, but the weight gain for the aluminide coating, after an initial lag, closely paralleled the weight gain of the uncoated material (see figure 5). This suggested that the glass and glass-on-aluminide coatings were effective at this temperature, but that the aluminide coating was not protective. The glass-on-aluminide coating did very well: even after 48 h the oxygen weight gain was less than  $35 \mu\text{g}/\text{cm}^2$ . If it is assumed that this represents oxygen permeation through the  $1.5\text{-}\mu\text{m}$ -thick glass layer, the oxygen weight gain corresponds to an oxygen diffusivity of roughly  $2.4 \times 10^{-14} \text{ cm}^2/\text{sec}$ , which is within an order of magnitude of the oxygen self-diffusion coefficient for fused quartz ( $3.5 \times 10^{-15} \text{ cm}^2/\text{sec}$ , ref 7).

The plastic elongations (see figure 6) confirmed, for the most part, the oxidation damage observed in the oxygen weight gains. However, the ductility of the aluminide coated material after 12 h is surprisingly high in light of its very large weight gain. This leads to the conclusion that most of the weight gain went into oxide formation, and that the portion that went into interstitial formation was actually quite low. In contrast, the ductility of the glass coated material was lower than weight gain would indicate. This leads to the conclusion that more interstitials were formed than weight gain accounted for. It is expected that where the glass and alloy were in direct contact, that the glass underwent a reduction reaction due to the high affinity of the alloy for oxygen. That oxygen then entered the alloy as interstitials contributing to the degradation of mechanical properties.

The plastic elongations of the glass-on-aluminide coated material were much better than

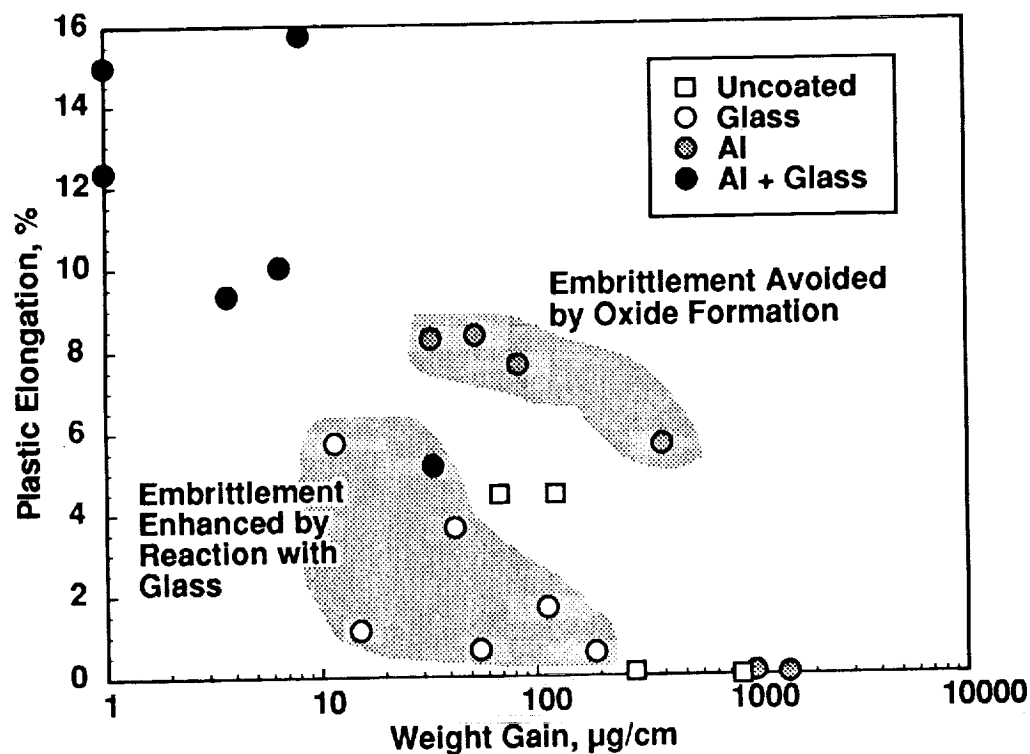


Figure 8. - Room temperature ductility after air exposures of coated Beta-21S.

that of the other coated materials, and in fact, rivaled those of Beta-21S vacuum annealed at this temperature (ca 16%, ref 3). This was attributed to the more complete exclusion of oxygen interstitials by the glass-on-aluminide coating. The micrographs in figure 7 reinforce this suggestion. At 800°C, it is expected that some alpha will be present. However, since oxygen is an alpha stabilizer, the presence of oxygen should cause additional alpha to form. The amounts of alpha are 7 vol% for the glass-on-aluminide-coated material, 10 vol% for the aluminide-coated material, and 21 vol% for the glass-coated material, indicating that the glass-on-aluminide-coated material has the least oxygen in solid solution.

The relationship between oxygen weight gain and plastic elongation is summarized for all the materials tested in figure 8. Grouped in one shaded region are cases where loss of ductility was observed at unexpectedly low oxygen weight gains. This was attributed to interstitials formed by reactions between the glass and the alloy. Grouped in the second shaded region are the cases where ductility was retained at unexpectedly large oxygen weight gains. This was attributed to competitive oxide formation preventing the formation of interstitials. All the glass-coated materials fall into group one and the aluminide-coated materials fall mostly in group two; which is reasonable given the function of these coatings.

The glass layer, in the glass-on-aluminide coatings, apparently blocks oxygen transport. If the aluminide layer were functioning as an oxygen trapping layer, then the glass-on-aluminide coatings would be grouped in figure 8 with the aluminide coatings. Actually, the glass-on-aluminide coatings behave more like the glass coatings: this suggests that

the function of the aluminide layer is that of a reaction barrier.

### Concluding Remarks

The results reported in this paper are significant in that they demonstrate the potential for practical coating systems that are very thin ( $< 3\text{-}\mu\text{m}$  thick), exclude oxygen from the alloy, and prevent unacceptable degradation of the mechanical properties. As a consequence, these coatings may find application in titanium alloy aerospace structures which are subject to high temperatures in service.

It was shown that uncoated Beta-21S, 4.5-mil sheet was embrittled at 700 and 800°C after only 12 h of exposure, but embrittlement was prevented by glass, aluminide, and glass-on-aluminide coatings less than  $3\text{-}\mu\text{m}$  thick. The glass-on-aluminide coating was the most successful with greater than 15% plastic elongation retained after 24 h at 800°C in air.

The glass and aluminide coatings functioned as protective layers in different ways: the glass by blocking transport, and the aluminide by trapping oxygen in the form of aluminum oxide. When used together in the glass-on-aluminide coating, the role of the aluminide appeared to be that of a barrier preventing interstitial-generating reactions between the glass and the Beta-21S alloy.

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